Electronic Supplementary Material (ESI) for Chemical Science.

Intra- and Intermolecular Interception of a Photochemically Generated Terminal Uranium Nitride

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General Considerations

All air- and moisture-sensitive operations were carried out in an MBraun drybox under an atmosphere of purified nitrogen or using high-vacuum standard Schlenk techniques. Dimethoxyethane (DME), diethyl ether (Et_2O), hexanes, pentane, and toluene were dried using a Pure Process Technology Solvent Purification System and subsequently stored under a dinitrogen atmosphere over activated 4 Å molecular sieves. All deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed by three freeze−pump−thaw cycles, and dried over activated 4 Å molecular sieves for 24 h prior to use. Celite and the 4 Å molecular sieves were heated to 150 °C for at least 24 h and then cooled under vacuum. $UI_3(dioxane)_{1.5}$,[1] $[K(DME)_2]_2L^{Ar}$,[2] $L^{Ar}UI(DME)$[2] and $LiNIm^{Dipp}$[3] were synthesized according to reported procedures. Ph_3CN_3 was synthesized from the reaction of Ph_3CCl with 10 equiv of NaN_3 in stirring THF for 24 h, filtered, and dried to give the product as a white solid. 2,6-dimethylphenyl isocyanide was purchased from Alfa Aesar and recrystallized from toluene prior to use. PMe_3 (99%) was purchased from Strem Chemical, Inc and was stored over 4 Å molecular sieves prior to use, while all other reagents were purchased from commercial suppliers and used as received. ^1H NMR spectra were recorded on a JEOL ECA 600 MHz or Bruker AVANCE III 400 MHz spectrometer. ^1H NMR spectra are referenced to $SiMe_4$ using the residual ^1H solvent peaks as internal standards. The $^{31}P\{^1H\}$NMR spectrum is referenced to external 85% H_3PO_4. IR data were collected using a Thermo Scientific Nicolet iS5 spectrometer. IR data of all samples were collected with powdered KBr, pressed into a pellet, and the data collected within a few minutes of sample preparation. The intensities are reported relative to the most intense peak and are given in parentheses using the following abbreviations: w = weak, m = medium, s = strong. UV-vis spectra were recorded on a NanBei NU-T6PC spectrophotometer and NIR spectra on a Cary 5000 spectrophotometer. Elemental analyses were performed by Midwest Microlabs, LLC.

Photochemical Reactions.

The photochemical experiments were performed using a LED bulb (365 nm) with the reaction samples positioned approximately 2 cm from the bulb. The light used in the photolysis experiments were Lixada 7W 25 LED bulbs purchased from Amazon.com, Inc. NMR and preparative scale experiments were performed in borosilicate glass tubes equipped with a J-Young valve. All experiments were cooled to room temperature using a stream of compressed air.

X-ray Structure Determination and Refinement.

Data for **1**·DME, **2**·C_6H_6, **3**·C_6H_{14}, **5**·Et_2O, and **6**·Et_2O.were collected on a 4-axis Bruker Venture D8 equipped with a HELIOS MX monochromator and Mo Kα IμS microfocus source (α = 0.71073 Å), while the data for **4**·Et_2O was collected on Bruker Quest D8 using a graphite monochromator with a Mo Kα sealed-tube X-ray source (α = 0.71073 Å). The crystals were mounted on a Mitigen Kapton loop or glass fiber coated in NVH oil and maintained at 100(2) K under a flow of nitrogen gas during data collection. Data collection and cell parameter determination were conducted using the SMART2 program.[4] Integration of the data and final cell parameter refinements were performed using SAINT3 software[5] with data absorption correction implemented through SADABS.[6] All Structures were solved using direct, intrinsic phasing, charge flipping and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXT, SHELXL and XT with the Olex2 crystallographic package.[7]

In **2**·C_6H_6, the azide unit exhibits positional disorder which was addressed by modelling the atoms in two positions with 50% occupancy. In **3**·C_6H_{14}, the co-crystallized molecule of hexane is highly disordered and was modelled in two major positions with atoms of the solvent molecule refined isotropically. Complex **5**·Et_2O crystallizes with two half molecules of Et_2O in its asymmetric unit with the atoms assigned 50% occupancy. In **6**·Et_2O, a methyl group of PMe_3 and an isopropyl substituent exhibit positional disorder which was addressed by modelling the atoms in two positions with 50% occupancy for the respective groups.

Complete crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC Nos. 1958453 (**1**·DME), 1958456 (**2**·C_6H_6), 1958640 (**3**·C_6H_{14}), 1958626 (**5**·Et_2O) and 1958455 **(6**·Et_2O).

Synthesis of $L^{Ar}U(NIm^{Dipp})$ (1).

To a 20 mL scintillation vial containing a small stir bar, $L^{Ar}UI(DME)$ (210 mg, 0.18 mmol) in DME (6 mL) was added. The solution was stirred for 5 min at which point $LiNIm^{Dipp}$ (76.4 mg, 0.18 mmol) was added as a solid. After stirring for 3 h, the solution colour turned dark brown and was accompanied by the formation of a colourless precipitate. The DME was removed under vacuum to give a brown powder. The material was dissolved in toluene (4 mL) and filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a dark brown filtrate. Removal of the toluene under vacuum gave a dark brown solid. The material was subsequently dissolved into DME (2 mL) and stored at -22 °C for 2 d to give dark brown crystals of **1**·DME. The crystals were washed with cold hexanes and dried. Yield: 85 mg, 36%. **^{1}H NMR (25 °C, 600 MHz, C_6D_6):** δ 61.59 (br s, 1H), 18.29 (s, 1H), 16.11(s, 1H), 14.50 (s,1H), 13.93 (s,1H), 13.28 (s, 1H), 11.88 (s, 1H), 11.21 (s, 1H), 9.86 (s, 3H), 9.72 (s, 1H), 8.90 (br s, 1H), 8.16 (s, 1H), 7.87 (br s, 3H), 7.83 (br s, 3H), 7.65 (s, 1H), 7.44 (s, 1H), 6.40 (s, 1H), 6.20 (s, 1H), 5.69 (s, 1H), 5.30 (s, 1H), 5.10 (s, 1H), 4.86 (s, 1H), 4.74 (s, 1H), 4.47 (s, 3H), 4.25 (s, 3H), 3.71(s, 1H), 3.41 (s, 3H), 3.29 (s, 1H), 3.08 (s, 1H), 2.93 (s, 1H), 2.82 (s, 3H), 2.37 (s, 1H), 2.14 (s, 1H), 1.68 (s, 3H), 1.40 (s, 1H), 1.29 (s, 3H), 1.22 (s, 1H), 1.16 (s, 1H), 0.99 (s, 1H), 0.82 (s, 1H), 0.68 (s, 1H), -0.31 (s, 3H), -0.46 (s, 3H), -1.01 (s, 3H), -1.91(s, 3H), -7.25(s, 3H), -15.71(s, 1H), -21.26 (s, 1H), -31.47 (br s, 1H), -39.84 (s, 3H). **IR (KBr pellet, cm^{-1}):** 439 (w), 479 (w), 513(w), 668 (w), 694 (w), 746 (s), 770(w), 790 (s), 847 (w), 887 (w), 899 (w), 934 (m), 1009 (w), 1058 (w), 1111 (m), 1174 (m), 1220 (w), 1267 (s), 1290 (m), 1309 (w), 1332 (m), 1362 (m), 1385 (m), 1427 (m), 1455 (s), 1524 (s), 1588 (m), 1632 (w), 2866 (m), 2926 (m), 2961 (s), 3052 (w), 3413(w). **UV-vis (C_6H_6, 0.075 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 282 (ε = 23,563). **NIR (C_6H_6, 2.0 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 1289 (sh, ε = 437), 920 (ε = 693), 803 (ε = 784), 696 (ε = 740). Anal. Calcd. for $C_{69}H_{82}N_5U$: C, 67.96; H, 6.78; N, 5.74. Found: C, 67.60; H, 7.39; N, 5.30.

Synthesis of $L^{Ar}U(N_3)(NIm^{Dipp})$ (2).

To a 20 mL scintillation vial containing a small stir bar, a solution of **1** (120 mg, 0.91 mmol) in toluene (4 mL) was added. The solution was stirred for 5 min at which point Ph_3CN_3 (26.1 mg, 0.91 mmol) was added as a solid. The reaction mixture was stirred for 1 h with the solution colour turning dark red-brown. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a dark brown filtrate. Removal of the toluene under vacuum gave a dark brown solid. The material was subsequently redissolved into toluene (0.5 mL) and one drop of benzene which was layered with hexanes (8 mL) and stored at -22 °C for 2 days to give dark brown crystals of **2**·C_6H_6. Crystals were washed with cold hexanes and dried. Yield: 70 mg, 57%. **^{1}H NMR (25 °C, 600 MHz, C_6D_6):** δ 27.78 (s, 1H), 15.49 (s, 1H), 14.86 (s, 1H), 14.53 (s, 1H), 13.68 (s, 1H), 12.01 (s, 1H), 11.82 (s, 1H), 9.86 (s, 3H), 8.71 (s, 1H), 8.53 (s, 1H), 8.27 (s, 1H), 7.90 (s, 1H), 7.67 (s, 3H), 7.56 (s, 3H), 6.98 (s, 1H), 6.70 (s, 1H), 6.62 (s, 1H), 6.19 (s, 1H), 6.06 (s, 1H), 5.88 (s, 1H), 5.53 (s, 1H), 5.35 (s, 1H), 4.95 (s, 1H), 4.58 (s, 3H), 4.36 (s, 3H), 4.03 (s, 1H), 3.71(s, 3H), 3.52 (s, 1H), 3.22 (s, 1H), 2.07 (s, 1H), 2.00 (s, 3H), 1.50 (s, 1H), 1.30 (s, 3H), 1.19 (s, 1H), 1.07 (s, 1H), 0.92 (s, 1H), 0.31 (s, 3H), 0.16 (s, 3H), -0.46 (s, 1H), -1.30 (s, 3H), -1.44 (s, 1H), -1.81 (s, 3H), -2.06 (s, 3H), -4.02 (s, 3H), -4.83 (s, 3H), -7.32 (s, 3H), -9.45 (s, 1H), -11.25 (s, 1H), -22.28 (s, 1H), resonances accounting for 3 protons not observed. **^{1}H NMR (25 °C, 600 MHz, toluene-*d*$_8$):** δ 28.88 (s, 1H), 15.92 (s, 1H), 15.66 (s, 1H), 14.80 (s, 1H), 13.85 (s, 1H), 12.00 (s, 1H), 10.22 (s, 1H), 9.87 (s, 1H), 8.92 (s, 1H), 8.29 (s, 1H), 7.86 (s, 1H), 7.77 (s, 3H), 7.69 (s, 1H), 7.40 (s, 3H), 7.26 (s, 1H), 6.68 (s, 1H), 6.55 (s, 1H), 6.38 (s, 1H), 6.09 (s, 1H), 5.94 (s, 1H), 5.75 (s, 1H), 5.58 (s, 1H), 5.29 (s, 1H), 5.11 (s, 1H), 4.65 (s, 3H), 4.52 (s, 1H), 4.02 (s, 1H), 3.47 (s, 3H), 3.17 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H), 1.69 (s, 1H), 1.59 (s, 1H), 1.49 (s, 1H), 1.32 (s, 1H), 1.27 (s, 3H), 1.10 (s, 1H), 0.97 (s, 1H), 0.26 (s, 3H), 0.08 (s, 3H), -0.82 (s, 1H), -1.64 (s, 3H), -1.76 (s, 3H), -2.07 (s, 3H), -4.18 (s, 3H), -5.22 (s, 3H), -7.45 (s, 3H), -8.90 (s, 1H), -11.98 (s, 1H), -22.28 (s, 1H). **IR (KBr pellet, cm^{-1}):** 435 (w), 478 (w), 591(w), 619 (w), 695 (w), 748 (m), 770(w), 790 (s), 850 (w), 907 (w), 933(w), 1006 (w), 1057 (w), 1101 (w), 1164 (w), 1220 (m), 1243 (m), 1284 (w), 1304 (w), 1332 (m), 1364 (m), 1383 (w), 1461 (s), 1509 (s), 1590 (m), 1631 (w), 2070 (υ_{N3}, m), 2867 (m), 2927 (m), 2961 (s), 3056 (w), 3413 (w). **UV-vis (C_6H_6, 0.065 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 281 (ε = 22,085). **NIR (C_6H_6, 1.85 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 1253 (ε = 66), 1219 (ε = 83), 1180 (ε = 63), 1006 (ε = 71), 710 (ε = 98). Anal. Calcd. for $C_{69}H_{82}N_8U\cdot C_6H_{14}$: C, 66.84; H, 7.18; N, 8.31. Found: C, 66.92; H, 7.08; N, 8.15.

Synthesis of (*N*-L^{Ar})U(NIm^{Dipp}) (3).

Complex **2** (70 mg, 0.52 mmol) was loaded into an NMR tube fitted with a J-young valve containing C_6D_6 (1 mL), and the solution was photolyzed at 365 nm for 10 d with the progress of the reaction monitored by ^{1}H NMR spectroscopy. After this time, the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a dark brown filtrate. Removal of the C_6D_6 under vacuum gave a dark brown solid. The material was subsequently dissolved into hexane (1 mL) and a few drops of Et_2O and one drop of C_6H_6 was add to it. The solution was stored at -22 °C for 3 days to give dark brown crystals of **3**·C_6H_{14}. Yield: 30 mg, 44%. **^{1}H NMR (25 °C, 600 MHz, C_6D_6)**: δ 97.06 (s, 1H), 62.26 (s, 1H), 42.71 (s, 1H), 31.71 (s, 1H), 20.62 (s, 1H), 19.91 (s, 1H), 18.75 (s, 1H), 17.96 (s, 1H), 16.54 (s, 1H), 12.90 (s, 1H), 12.02 (s, 1H), 10.61 (s, 1H), 9.97 (s, 3H), 9.28 (s, 1H), 8.80 (s, 1H), 8.56 (s, 1H), 6.04 (s, 1H), 4.59 (s, 3H), 4.32 (s, 3H), 3.74 (s, 1H), 2.29 (s, 1H), 2.05 (s, 1H), 0.87 (s, 3H), 0.51 (s, 1H), 0.34 (s, 1H), 0.06 (s, 3H), -0.50 (s, 1H), -0.65 (s, 1H), -0.83 (s, 3H), -1.18 (s, 3H), -1.94 (s, 3H), -3.03 (s, 3H), -3.98 (s, 1H), -4.40 (s, 1H), -4.59 (s, 3H), -4.83 (s, 1H), -5.20 (s, 3H), -5.39 (s, 3H), -5.84 (s, 1H), -6.76 (s, 1H), -12.03 (s, 3H), -13.05 (s, 1H), -13.30 (s, 1H), -13.87 (s, 1H), -20.20 (s, 3H), -22.30 (s, 1H), -24.51 (s, 3H), -25.95 (s, 3H), -28.24 (s, 1H), -56.64 (s, 1H). **IR (KBr pellet, cm^{-1}):** 438 (w), 587 (w), 668 (w), 748 (m), 795 (w), 809 (w), 839 (w), 914 (w), 934 (w), 1006 (w), 1058 (w), 1171 (m), 1224 (w), 1259 (w), 1304 (m), 1332 (w), 1363 (w), 1383 (w), 1473 (m), 1491 (m), 1517 (w), 1632 (m), 2058 (w), 2359 (w), 2868 (m), 2927 (m), 2962 (s), 3064 (w), 3416 (w). **UV-vis (C_6H_6, 0.063 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 314 (ε = 13,051), 280 (ε = 19,892). **NIR (C_6H_6, 1.25 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 1189 (ε = 53), 1107 (ε = 48), 1028 (ε = 35), 697 (ε = 71). Anal. Calcd for $C_{69}H_{82}N_6U{\cdot}C_6H_6$: C, 68.68; H, 6.76; N, 6.41. Found: C, 68.17; H, 6.52; N, 6.63.

Synthesis of (CO-L^{Ar})U(N_3)(NIm^{Dipp}) (4).

Complex **2** (50 mg, 0.37 mmol) was loaded into an NMR tube fitted with a J-young valve containing C_6H_6 (1.5 mL), and the solution was then frozen with liquid nitrogen and left for 5 min under vacuum then backfilled with CO (1 atm). The solution was then placed on a rotary spinner and left to mix for 12 h, during which the reaction mixture turned purple-brown. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a purple-brown filtrate. Removal of the C_6H_6 under vacuum gave a purple-brown solid. The material was subsequently redissolved into hexane (2 mL) and Et_2O (1 mL) and stored at -22 °C for 2 d to give yellow coloured crystals of **4**·Et_2O. Yield: 10 mg, 19%. **^{1}H NMR (25 °C, 400 MHz, C_6D_6):** δ 75.58 (s, 3H), 36.50 (s, 3H), 30.00 (s, 3H), 28.55 (s, 1H), 25.52 (s, 3H), 20.86 (s, 1H), 18.02 (s, 1H), 15.42 (s, 1H), 13.41 (s, 1H), 10.59 (s, 3H), 9.60 (s br, 6H), 8.80 (s, 1H), 7.76 (s, 1H), 6.44 (s, 1H), 6.22 (s, 1H), 6.11 (s, 1H), 5.95 (s, 1H), 5.42 (s, 1H), 3.76 (s, 1H), 3.27 (s, 3H), 2.92 (s, 3H), 2.72 (s, 1H), 2.43 (s, 1H), 2.29 (s, 1H), 1.12 (br, 3H), 0.35 (s, 3H), 0.20 (s, 3H), 0.05 (s, 1H), -1.31 (s, 3H), -1.75 (s, 1H), -1.99 (s, 1H), -2.83 (s, 3H), -3.20 (s, 3H), -3.95 (s, 1H), -4.24 (s, 1H), -4.71 (s, 1H), -5.65 (s, 1H), -6.47 (s, 1H), -9.22 (s, 1H), -9.67 (s, 1H), -10.18 (s, 3H), -11.94 (s, 1H), -13.62 (s, 1H), -14.16 (s, 1H), -15.94 (s, 1H), -24.98 (s, 1H), -29.53 (s, 1H), -37.30 (s, 1H), -40.07 (s, 1H), -43.64 (s, 1H). Multiple attempts to isolate pure samples of **4** for elemental analysis failed due to the persistent co-crystallization of small, unidentified paramagnetic impurities.

Synthesis of (L^{Ar})U[NCN($C_6H_3Me_2$)](NIm^{Dipp}) (5).

Complex **2** (60 mg, 0.44 mmol) was loaded into an NMR tube fitted with a J-young valve and to this was added 2,6 dimethylphenyl isocyanide (5.9 mg, 0.44 mmol) in C_6D_6 (1 mL). The solution was photolyzed at 365 nm for 10 d with the progress of the reaction monitored by ^{1}H NMR spectroscopy, during which time the solution turned a dark purple. This solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a dark purple filtrate. Removal of the C_6D_6 under vacuum gave a dark purple solid. The material was subsequently dissolved into hexanes (1.5 mL) and Et_2O (0.5 mL) with 1 drop of DME and stored at -22 °C for 4 d to give purple crystals of **5**·Et_2O. Yield: 40 mg, 44%. **^{1}H NMR (25 °C, 600 MHz, C_6D_6):** δ 45.87 (s, 1H), 22.77 (s, 1H), 21.11 (s, 1H), 20.69 (s, 1H), 16.45 (s, 1H), 14.07 (s, 1H), 11.61 (s, 1H), 11.13 (s, 1H), 10.63 (s, 3H), 10.47 (s, 3H), 10.33 (s, 1H), 9.31 (s, 1H), 9.14 (s, 1H), 8.40(s, 1H), 8.20 (s, 1H), 8.11 (s, 1H), 7.86 (s, 3H), 7.75 (s, 1H), 7.02 (s, 1H), 6.79 (s, 1H), 6.51 (s, 1H), 6.14 (s, 1H), 5.91 (s, 1H), 5.85 (s, 1H), 5.63 (s, 1H), 5.38 (s, 1H), 5.28 (s, 1H), 5.16 (s, 1H), 5.13 (s, 1H), 4.98 (s, 1H), 4.47 (s, 1H), 4.23 (s, 3H), 4.07 (s, 3H), 2.19 (s, 1H), 2.11 (s, 1H), 1.61 (s, 3H), 1.12 (s, 1H), 0.99 (s, 3H), 0.78(s, 3H) , 0.62 (s, 3H), 0.43 (s, 3H), -0.65 (s, 3H), -1.55 (s, 3H), -2.18 (s, 3H), -3.29 (s, 1H), -3.68 (s, 3H), -5.03 (s, 1H), -5.17 (s, 3H), -6.22 (s, 1H), -6.59 (s, 3H), -6.70 (s, 3H), -11.57 (s, 1H), -14.61 (s, 3H), -21.11 (s, 1H), -25.28 (s, 1H). **IR (KBr pellet, cm^{-1}):** 419 (w), 425 (w), 605 (w), 631 (w), 700 (m), 730 (w), 749 (s), 809 (w), 840 (w), 915 (w), 934 (w), 1006 (w), 1057 (w), 1104 (w), 1179 (w), 1236 (w), 1283 (m), 1303 (m), 1329 (m), 1362 (m), 1383 (m), 1473 (s), 1490 (s), 1550 (w), 1576 (m), 1601 (m), 1617 (s), 2100 (m), 2867 (m), 2926 (m), 2960 (s), 3057 (w), 3421 (w). **UV-vis (C_6H_6, 0.053 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 317 (ε = 16,220), 280 (ε = 24,228). **NIR (C_6H_6, 1.84 mM, 25 °C, L·mol^{-1}·cm^{-1}):** 1208 (ε = 72), 1101 (ε = 74), 1171 (ε = 64), 1149 (ε = 64), 701 (ε = 143). Anal. Calcd. for $C_{78}H_{91}N_7U·Et_2O$: C, 67.70; H, 7.00; N, 6.74. Found: C, 67.27; H, 6.76; N, 6.29.

Synthesis of (*N*,*C*-L^{Ar*})U(N=PMe$_3$)(NIm^{Dipp}) (6).
Complex **2** (60 mg, 0.44 mmol) was loaded into an NMR tube fitted with a J-young valve and to this was added PMe_3 (6 mg, 8 mL, 0.78 mmol) in C_6D_6 (1 mL). The sample was photolyzed at 400 nm for 2 d, during which time the reaction colour changed to light brown. The solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool to give a dark brown filtrate. Removal of the C_6D_6 under vacuum gave a dark brown solid. The material was subsequently dissolved into hexanes (1.5 mL) and Et_2O (0.5 mL) and stored at -30 °C for 4 d to give yellow-brown crystals of **6**·Et_2O. Yield: 9 mg, 15%. **^{1}H NMR (25 °C , 600 MHz, C_6D_6)**: δ 45.22 (s, 1H), 39.44 (s, 1H), 32.95 (s, 1H), 31.31 (s, 1H), 24.80 (s, 1H), 12.72 (s, 1H), 12.11 (s, 1H), 8.18 (s, 1H), 8.05 (s, 3H), 7.83 (s, 3H), 7.71 (s, 1H), 7.54 (s, 3H), 7.23 (s, 3H), 7.11 (s, 3H), 6.86 (s, 3H), 6.75 (s, 3H), 6.51 (s, 3H), 6.27 (s, 1H), 5.99 (s, 1H), 5.93 (s, 1H), 5.75 (s, 1H), 5.63 (s, 1H), 5.50 (s, 1H), 4.65 (s, 1H), 4.24 (s, 1H), 3.35 (s, 3H), 2.98 (s, 1H), 2.85 (s, 1H), 2.71 (s, 1H), 2.45 (s, 1H), 1.73 (s, 3H), 1.51 (s, 3H), 1.33 (s, 3H), 1.19 (s br, 3H), 1.07 (s br, 3H), 0.93 (s br, 3H), 0.31 (s, 1H), -0.05 (s, 1H), -0.64 (s, 1H), -1.67 (s, 1H), -2.21 (s, 1H), -3.23 (s, 1H), -3.35 (s, 3H), -3.58 (s, 1H), -3.68 (s, 1H), -6.09 (s, 1H), -6.40 (s, 1H), -8.28 (s, 3H), -9.21 (s, 1H), -11.98 (s, 3H), -22.45 (s, 3H). **^{31}P{^{1}H} NMR (25 °C , 600 MHz, C_6D_6)**: δ 12.12. **IR (KBr pellet, cm^{-1}):** 3412 (w), 3058 (w), 2961 (s), 2962 (m), 2867 (m), 2057 ($\upsilon_{P=N}$, w), 1634 (m), 1600 (m), 1576 (m), 1558 (w), 1539 (w), 1490 (m), 1472 (s), 1383 (w), 1362 (m), 1306 (w), 1260 (m), 1104(w), 1051 (m), 1031 (m), 1006 (w), 934 (w), 914(w), 856(w), 808 (m), 747 (m), 700 (m), 654 (w).

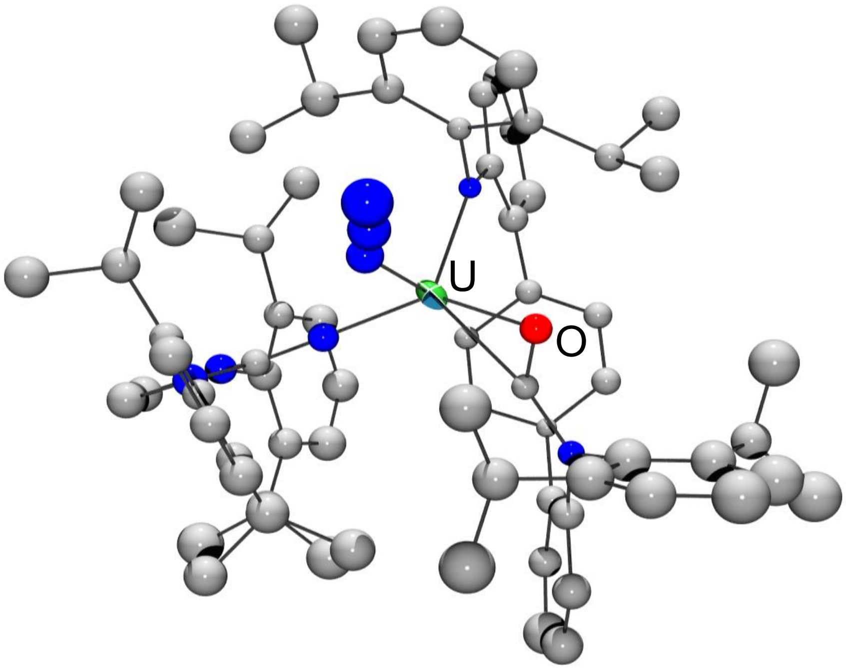

Figure SI1. Molecular structure diagram of **4** from X-ray diffraction analysis presented to demonstrate connectivity. Hydrogen atoms and co-crystallized molecule of Et_2O are omitted for clarity.

Table S1. X-ray Crystallographic Data for **1**·DME, **2**·C_6H_6, **3**·C_6H_{14}, **5**·Et_2O and **6**·Et_2O.

	1·DME	**2**·C_6H_6
empirical formula	$C_{73}H_{92}N_5O_2U$	$C_{75}H_{88}N_8U$
crystal habit, colour	block, red brown	plate, red
crystal size (mm)	0.42 × 0.41 × 0.34	0.42 × 0.38 × 0.32
crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Volume (Å^3)	3230.4(4)	3230.5(2)
a (Å)	13.2857(9)	13.1219(4)
b (Å)	13.9411(8)	13.5561(5)
c (Å)	20.5686(2)	20.3099(7)
α (deg)	103.573(2)	78.109(2)
β (deg)	95.666(3)	76.264(2)
γ (deg)	116.252(2)	68.201(2)
Z	2	2
formula weight (g/mol)	1309.54	1339.56
density (calculated) (mg/m^3)	1.346	1.377
absorption coefficient (mm^{-1})	2.561	2.561
F_{ooo}	1346.0	1372.0
Total no. reflections	66208	95837
Unique reflections	18590	10999
final R indices [I > 2σ(I)]	R_1 = 0.0471, wR_2 = 0.960	R_1 = 0.0464, wR_2 = 0.0985
largest diff. peak and hole (e^- Å^{-3})	1.55 and -1.74	2.67 and -1.75
GOF	1.021	1.134

	3•C_6H_{14}	**5**•Et_2O
empirical formula	$C_{75}H_{96}N_6U$	$C_{82}H_{101}N_7OU$
crystal habit, colour	plate, red	block, brownish red
crystal size (mm)	0.33 × 0.32 × 0.27	0.35 × 0.32 × 0.28
crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Volume ($Å^3$)	6994.8(6)	3692.6(3)
a (Å)	14.7113(8)	13.1812(5)
b (Å)	12.9790(6)	15.8571(6)
c (Å)	36.7480(2)	19.6743(8)
α (deg)	90	110.710(2)
β (deg)	94.521(2)	90.480(2)
γ (deg)	90	105.002(2)
Z	4	2
formula weight (g/mol)	1319.60	1438.72
density (calculated) (mg/m^3)	1.253	1.294
absorption coefficient (mm^{-1})	2.364	2.246
F_{ooo}	2720.0	1484.0
Total no. reflections	233359	99947
Unique reflections	18690	14040
final R indices [I > 2σ(I)]	$R_1 = 0.0394$, $wR_2 = 0.0850$	$R_1 = 0.0326$, $wR_2 = 0.0846$
largest diff. peak and hole ($e^- Å^{-3}$)	1.28 and -1.75	1.63 and -0.64
GOF	1.178	1.077

	6•Et_2O
empirical formula	$C_{76}H_{99}N_6OPU$
crystal habit, colour	needle, brownish yellow
crystal size (mm)	0.24 × 0.23 × 0.15
crystal system	monoclinic
Space group	$P2_1/c$
Volume ($Å^3$)	7197(3)
a (Å)	25.884(5)
b (Å)	13.889(3)
c (Å)	21.315(4)
α (deg)	90
β (deg)	110.09(3)
γ (deg)	90
Z	4
formula weight (g/mol)	1381.61
density (calculated) (mg/m^3)	1.275
absorption coefficient (mm^{-1})	2.323
F_{ooo}	2848.0
Total no. reflections	119106
Unique reflections	18514
final R indices [I > 2σ(I)]	$R_1 = 0.0273$, $wR_2 = 0.0604$
largest diff. peak and hole ($e^- Å^{-3}$)	0.56 and -0.70
GOF	1.020

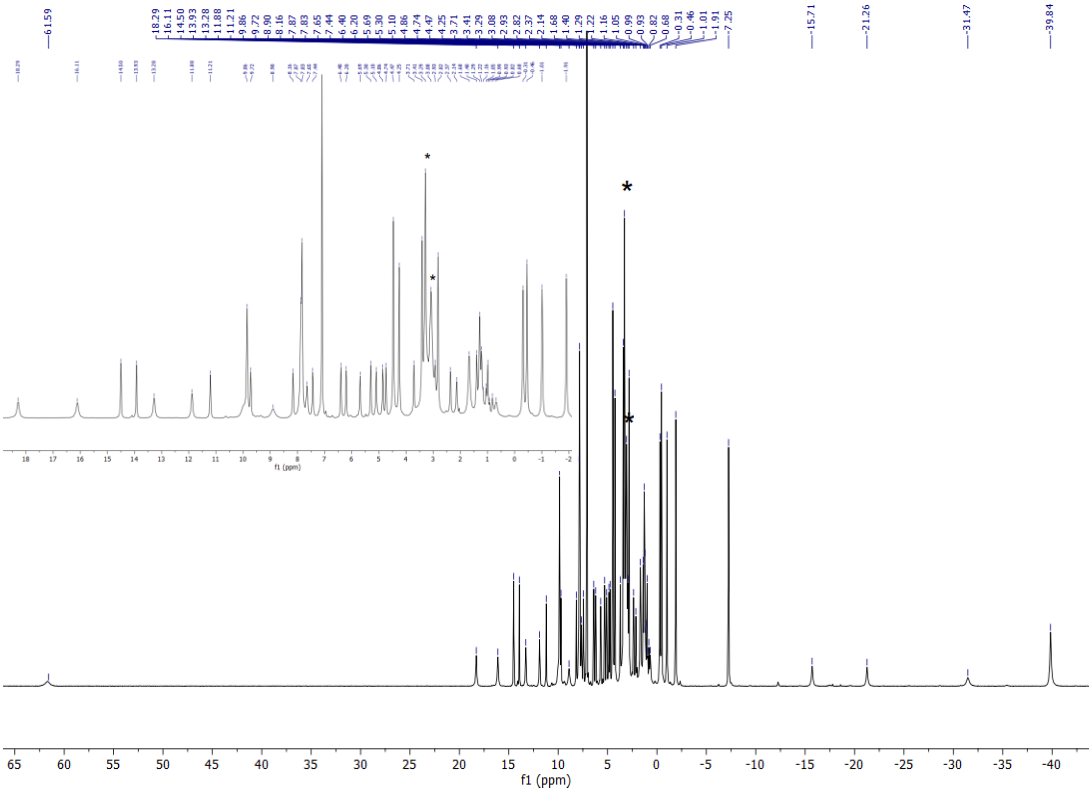

Figure SI2. ^{1}H NMR spectrum of **1**·C_6H_6 in C_6D_6 at 25 °C. Asterisks denote the presence of residual DME.

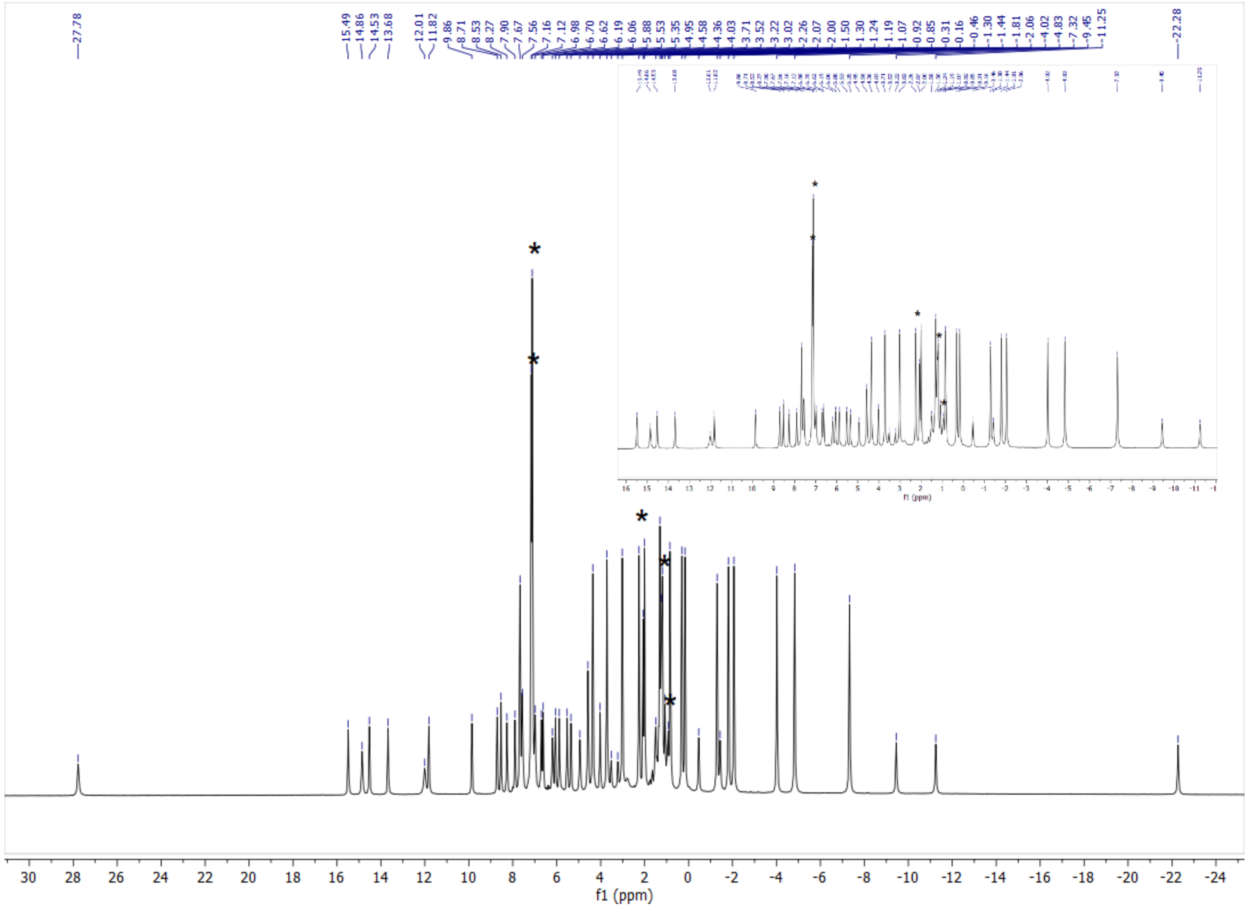

Figure SI3. ^{1}H NMR spectrum of **2**·C_6H_6 in C_6D_6 at 25 °C. Asterisks denote the presence of residual toluene and hexanes.

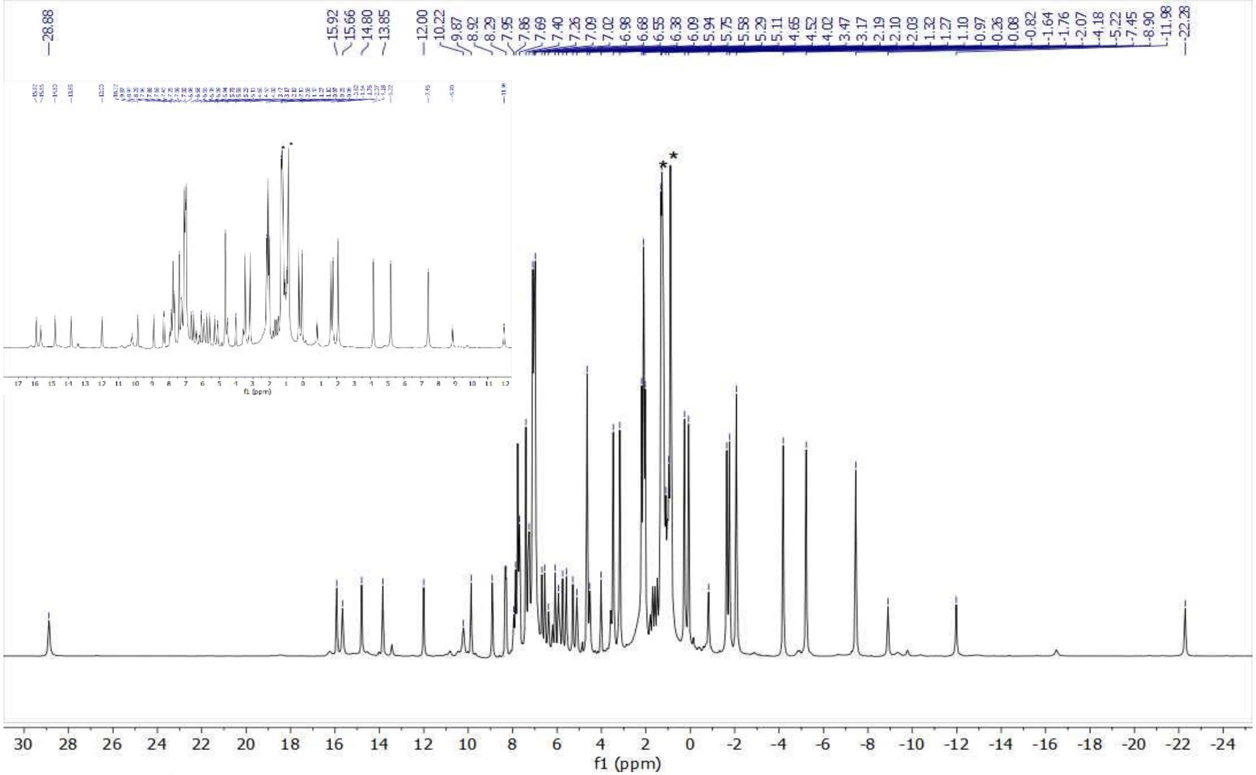

Figure SI4. ^{1}H NMR spectrum of **2**·C_6H_6 in toluene-d_8 at 25 °C. Asterisks denote the presence of residual hexanes.

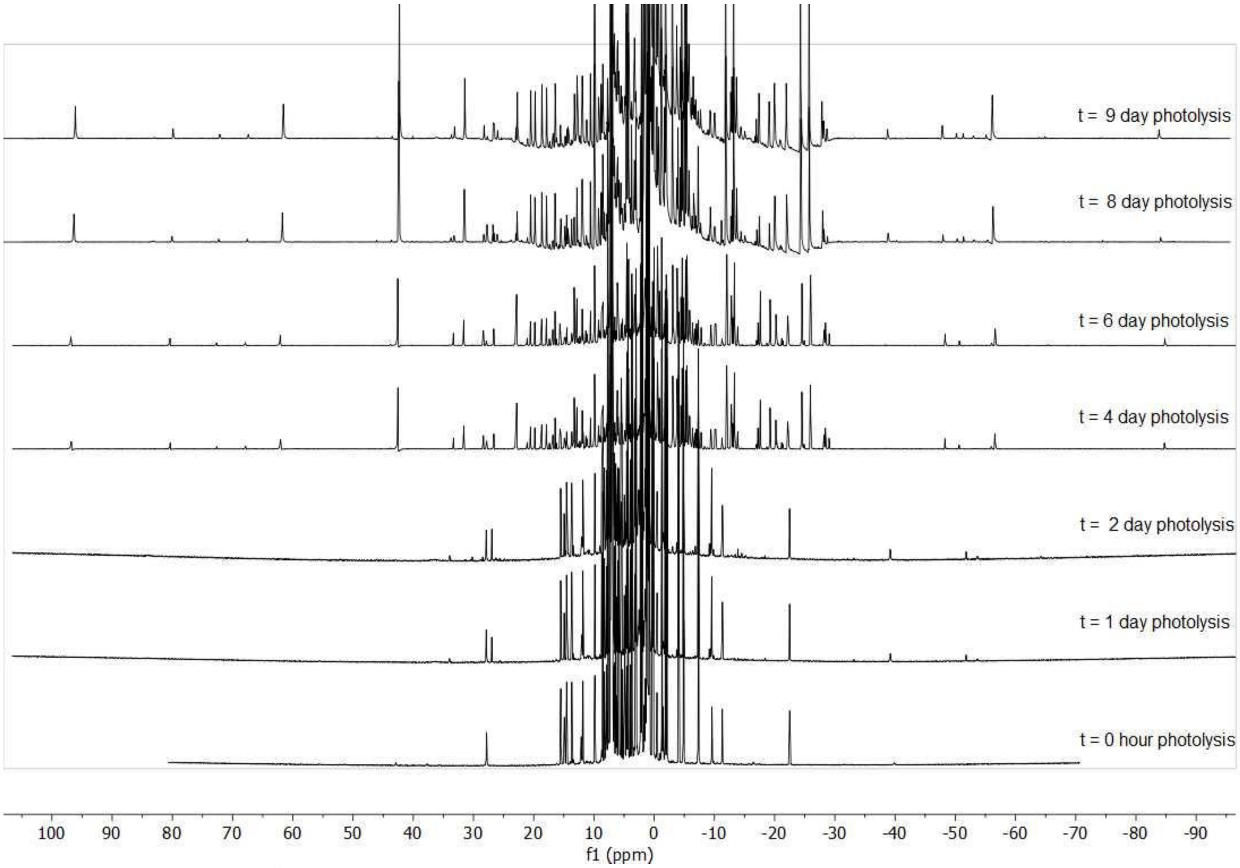

Figure SI5. Stacked ^{1}H NMR (25 ˚C, 600 MHz, C_6D_6) spectral plot following the photochemical conversion of **2**·C_6H_6 to **3**.

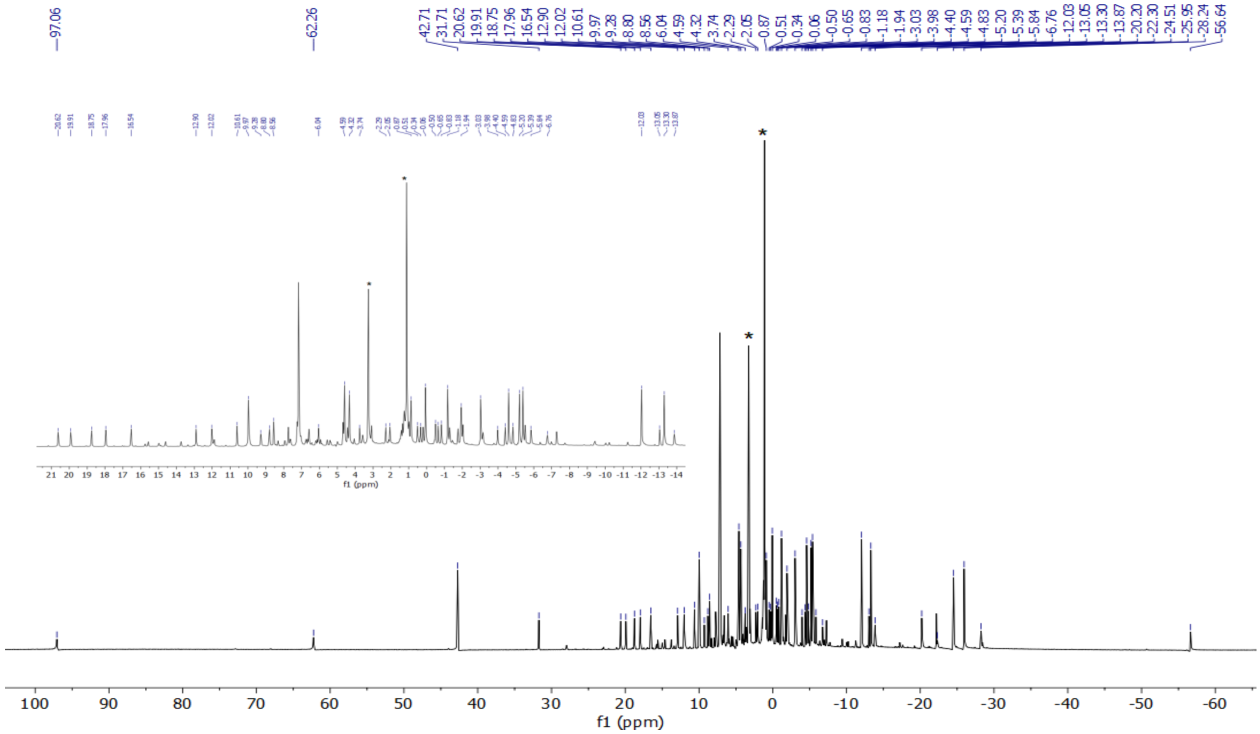

Figure SI6. ^{1}H NMR spectrum of **3**·C_6H_{14} in C_6D_6 at 25 °C. Asterisks denote the presence of residual diethyl ether.

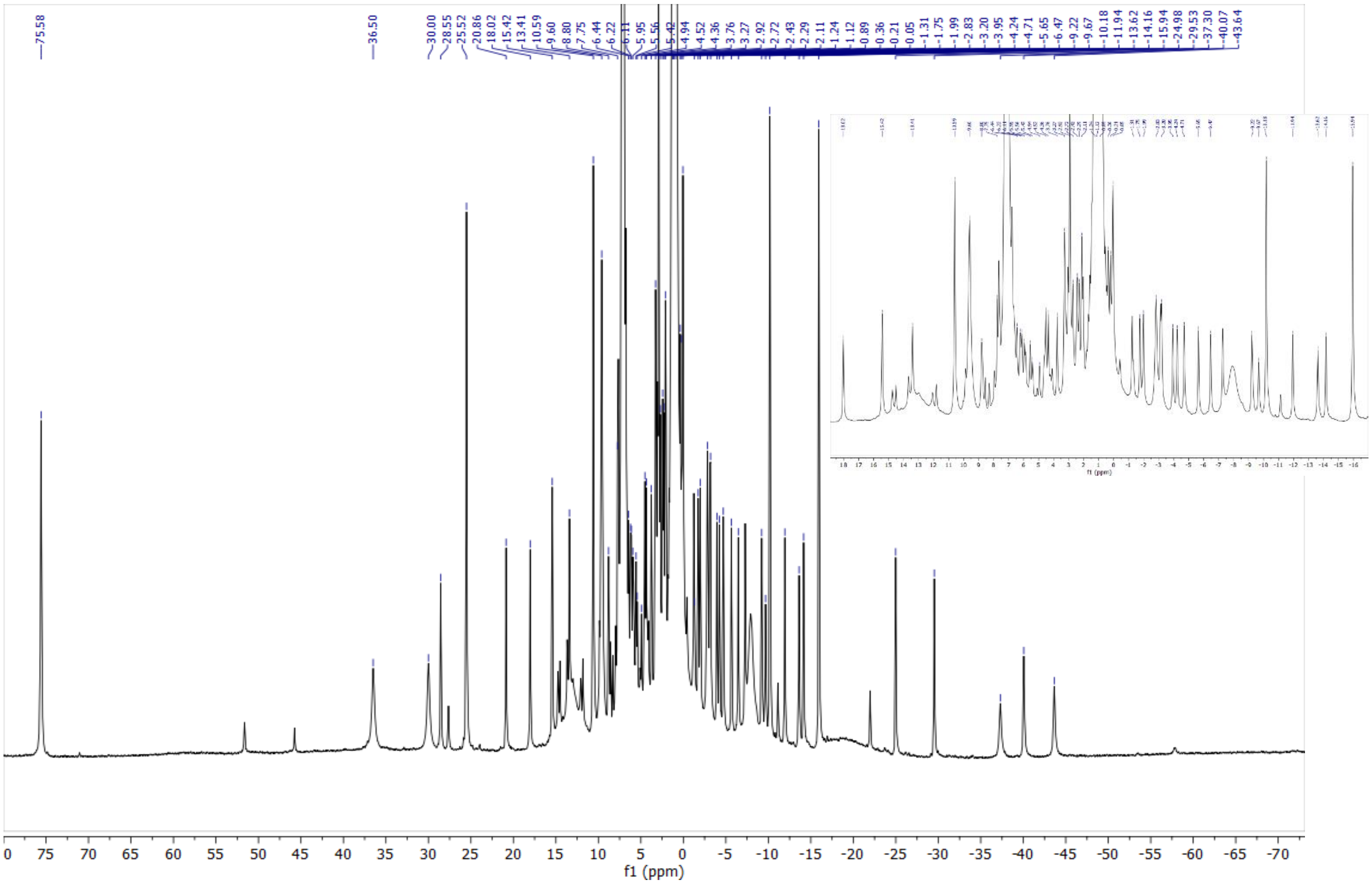

Figure SI7. ^{1}H NMR spectrum of **4**·Et$_2$O in C$_6$D$_6$ at 25 °C. The spectrum presents resonances attributable to other paramagnetic impurities. Only those resonances corresponding to **4** are labelled.

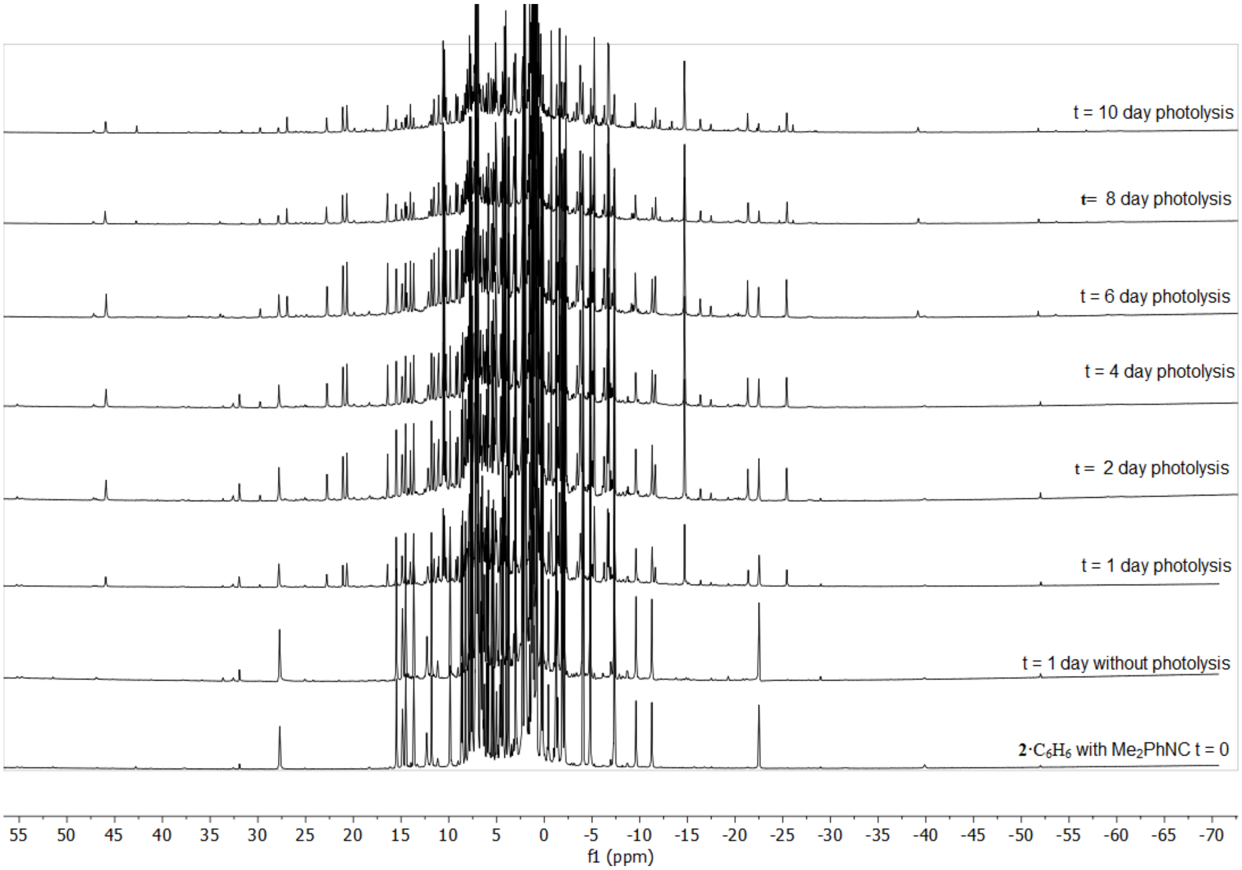

Figure SI8. Stacked ^{1}H NMR (25 ˚C, 600 MHz, C_6D_6) spectral plot following the photochemical conversion of **2**·C_6H_6 to **5** in the presence of $C{\equiv}N(C_6H_3Me_2)$.

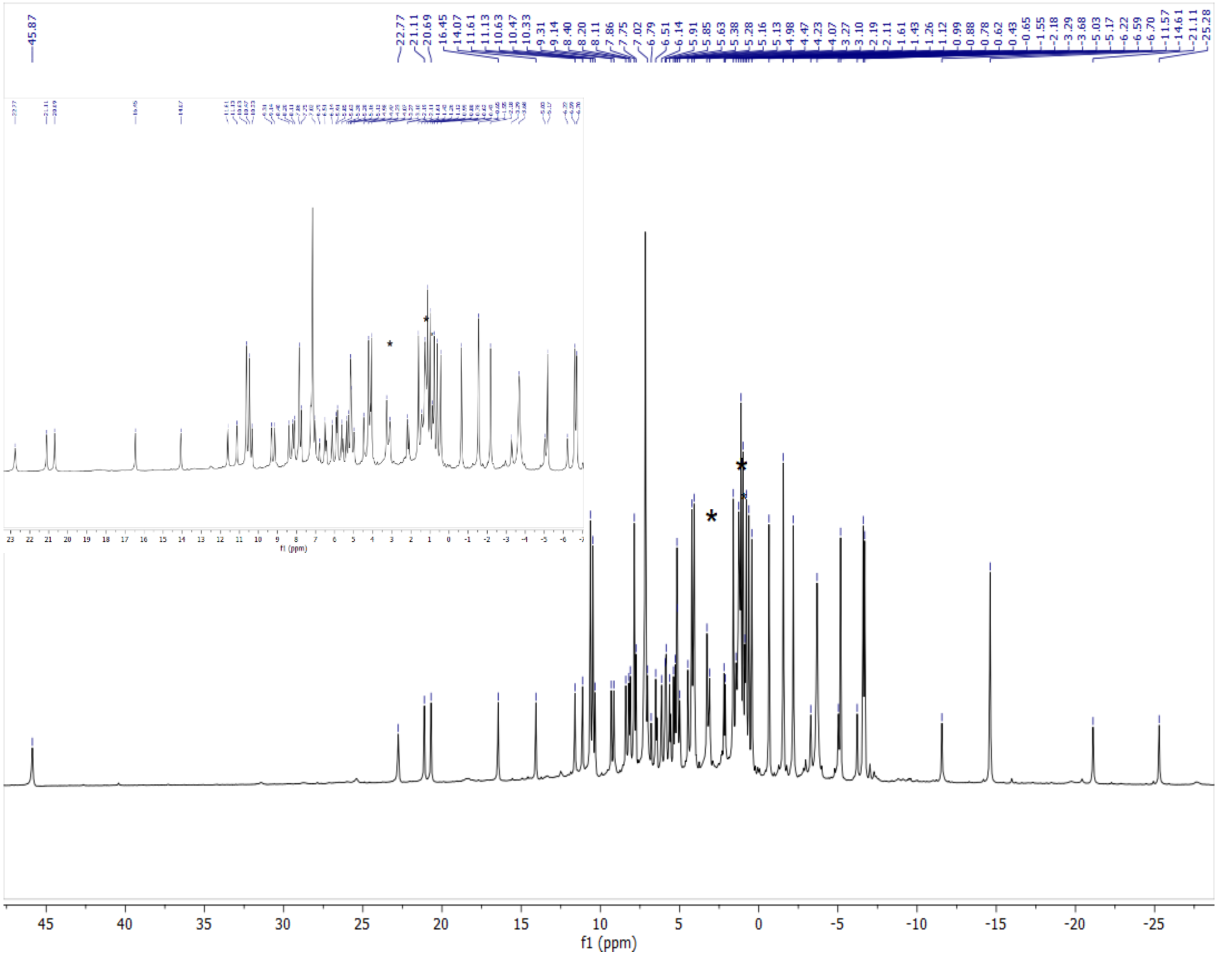

Figure SI9. ^{1}H NMR spectrum of **5**·Et$_2$O in C_6D_6 at 25 °C. Asterisks denote the presence of residual DME and hexanes.

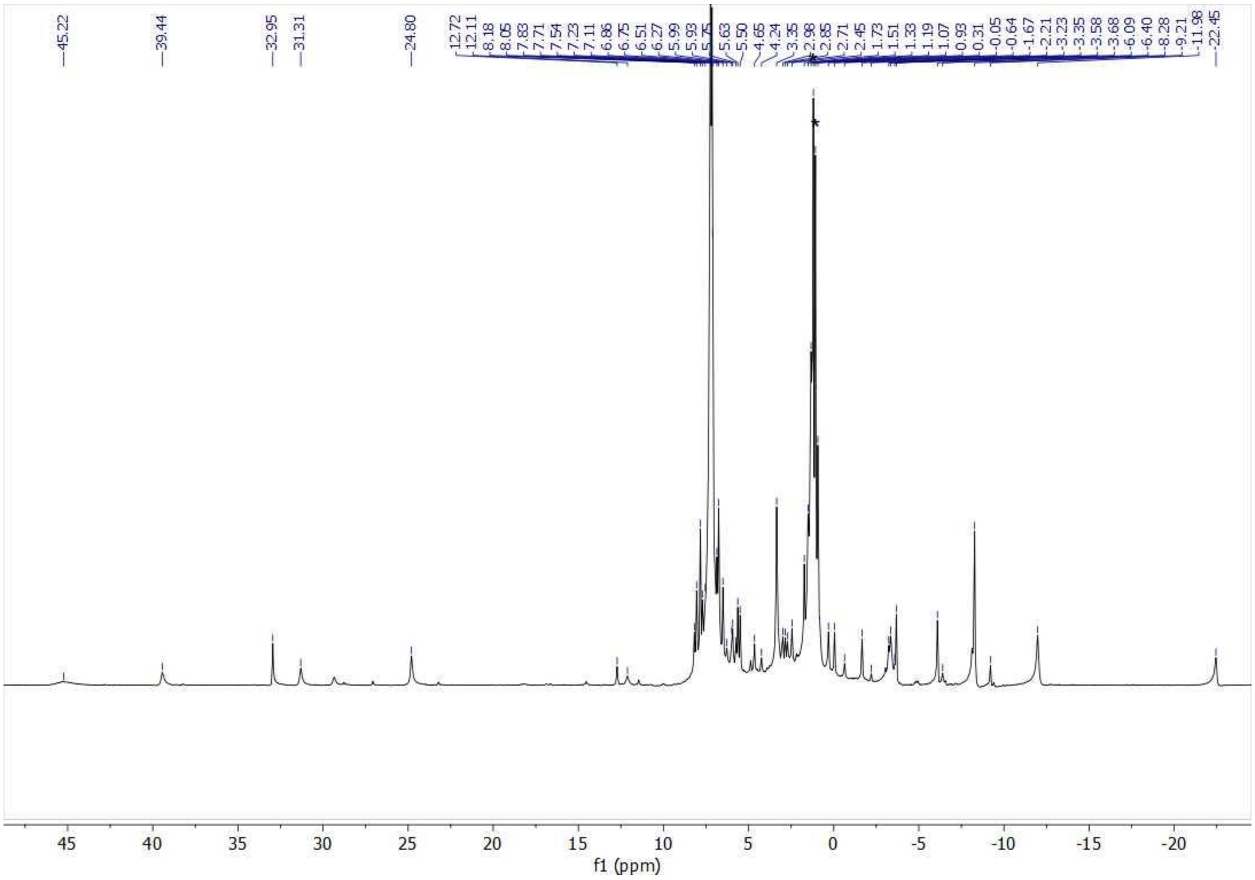

Figure SI10. ^{1}H NMR spectrum of **6**·Et$_2$O in C_6D_6 at 25 °C. Asterisks denote the presence of residual hexanes.

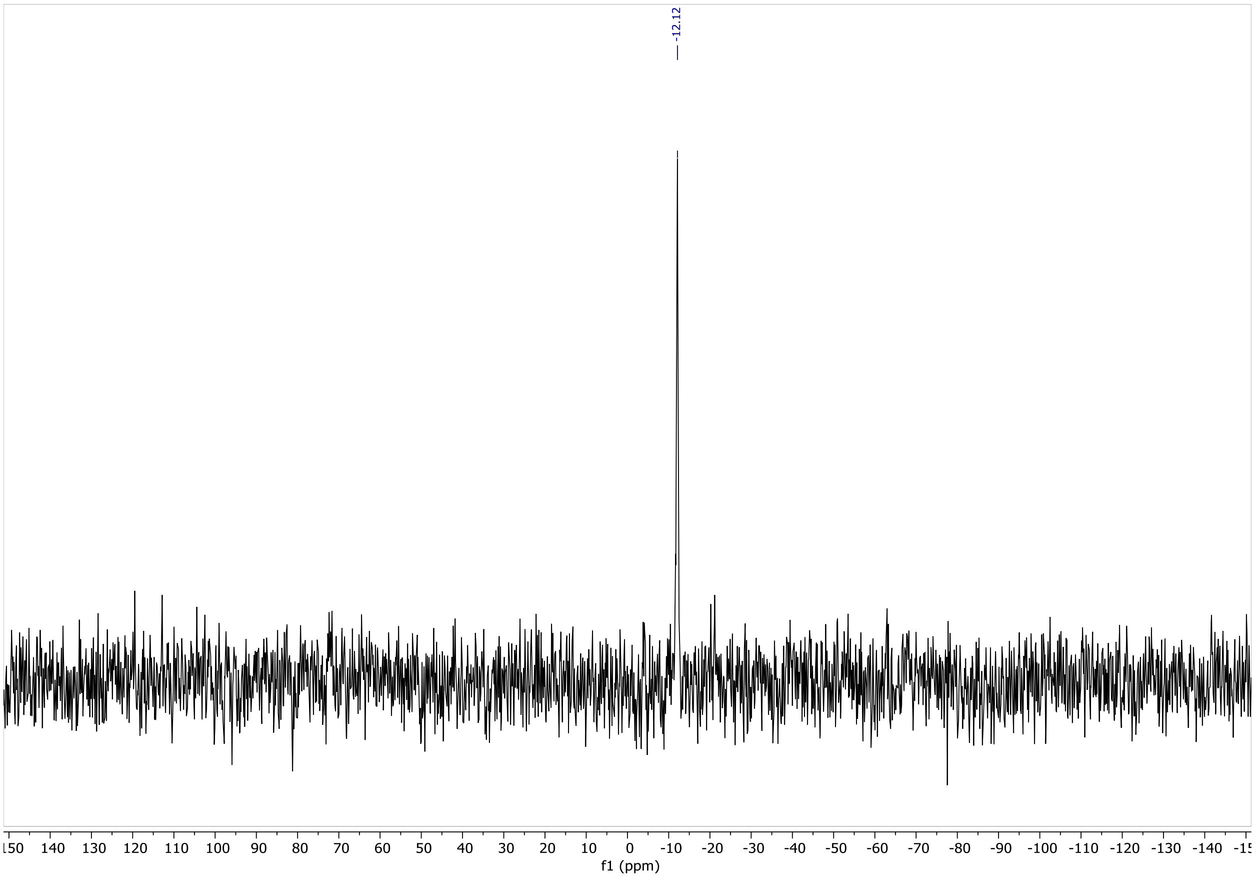

Figure SI11. $^{31}P\{^{1}H\}$ NMR spectrum of **6**·Et_2O in C_6D_6 at 25 °C.

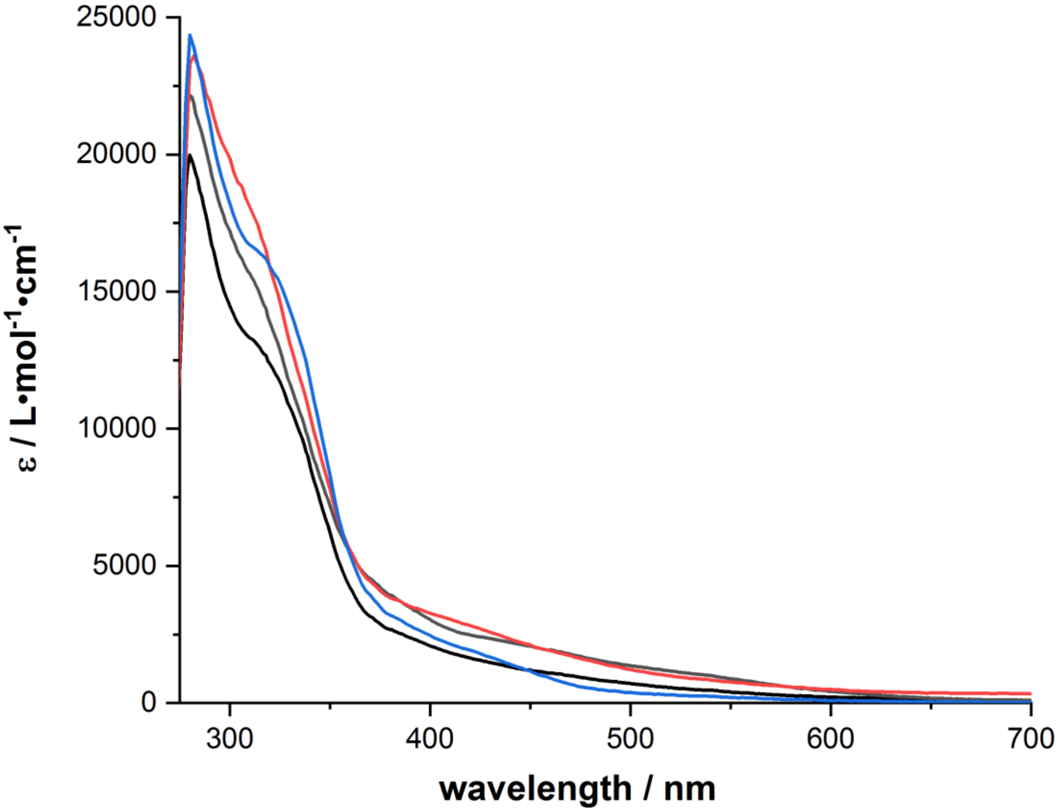

Figure SI12. Room temperature UV-vis absorption spectra of **1** (0.075 mM; red), **2** (0.065 mM; green), **3** (0.063 mM; black), and **5** (0.053 mM; blue) in benzene.

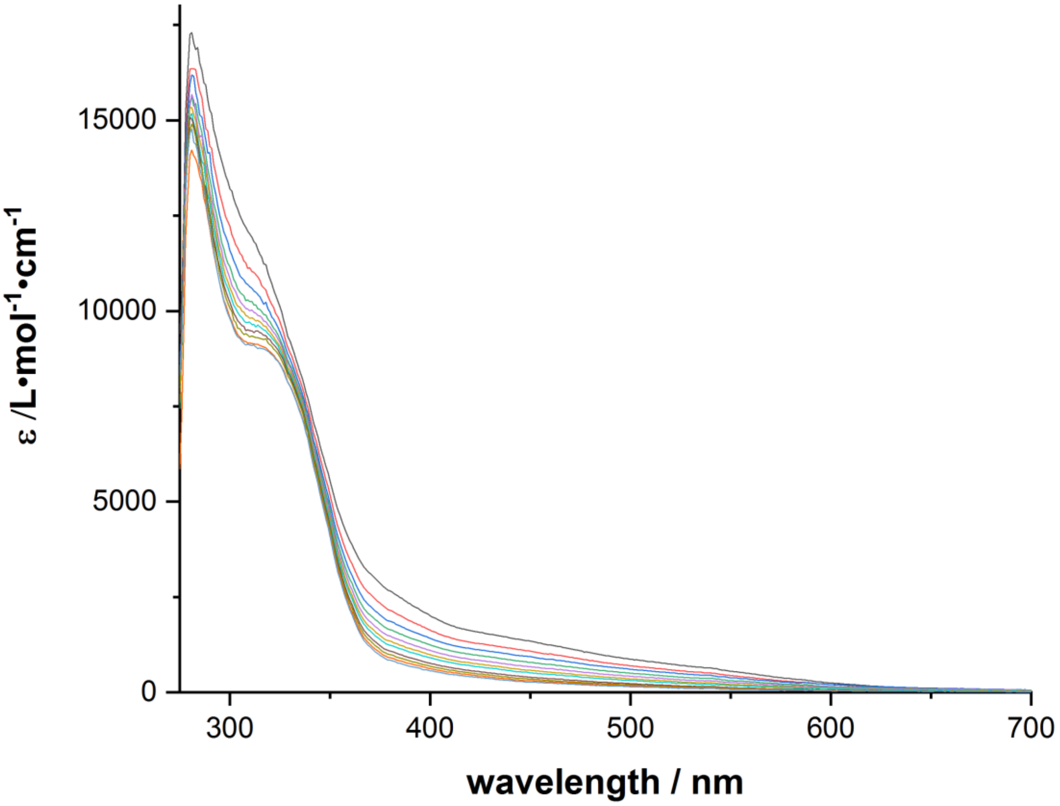

Figure SI13. UV-vis absorption spectra of the photochemical transformation of **2** (0.116 mM) converting to **3** in benzene at room temperature.

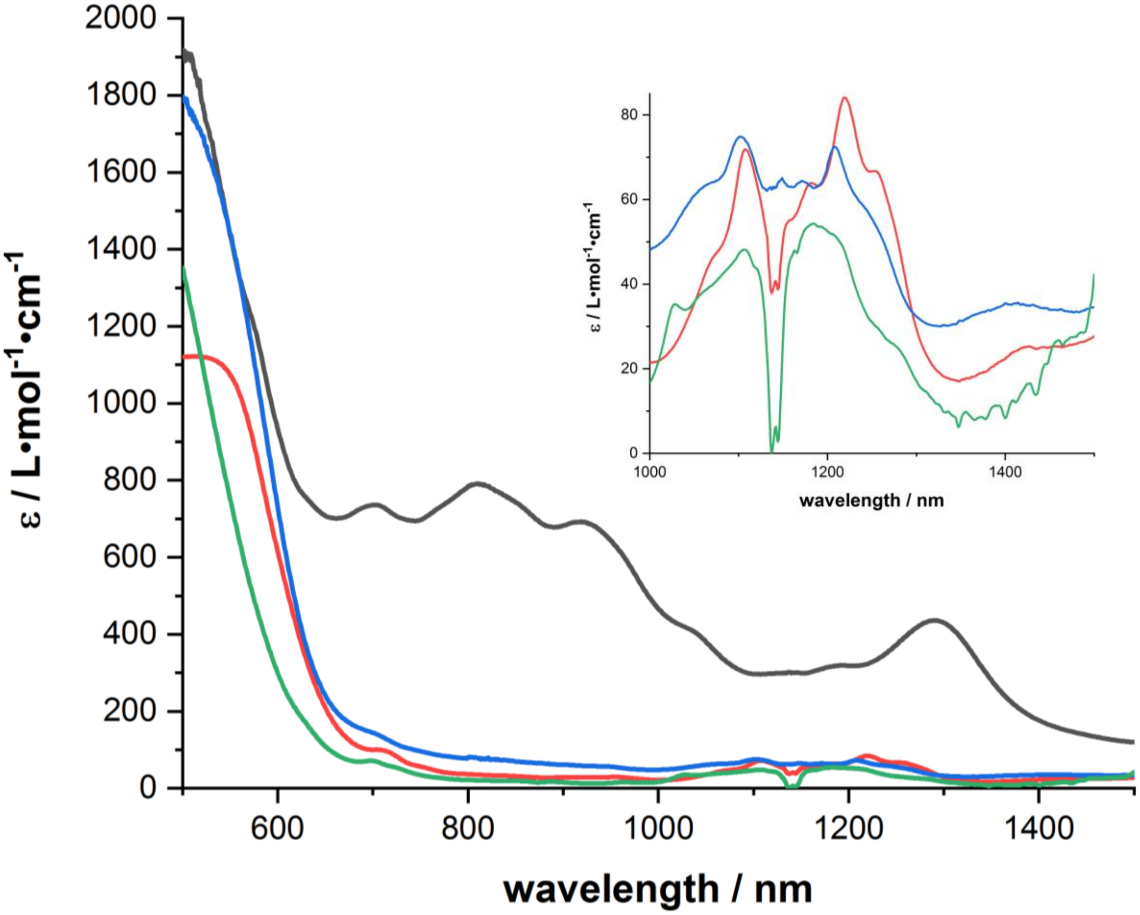

Figure SI14. Room temperature NIR absorption spectra for **1** (2.0 mM; black), **2** (1.85 mM; red), **3** (1.25 mM; green), and **5** (1.84 mM; blue) in benzene.

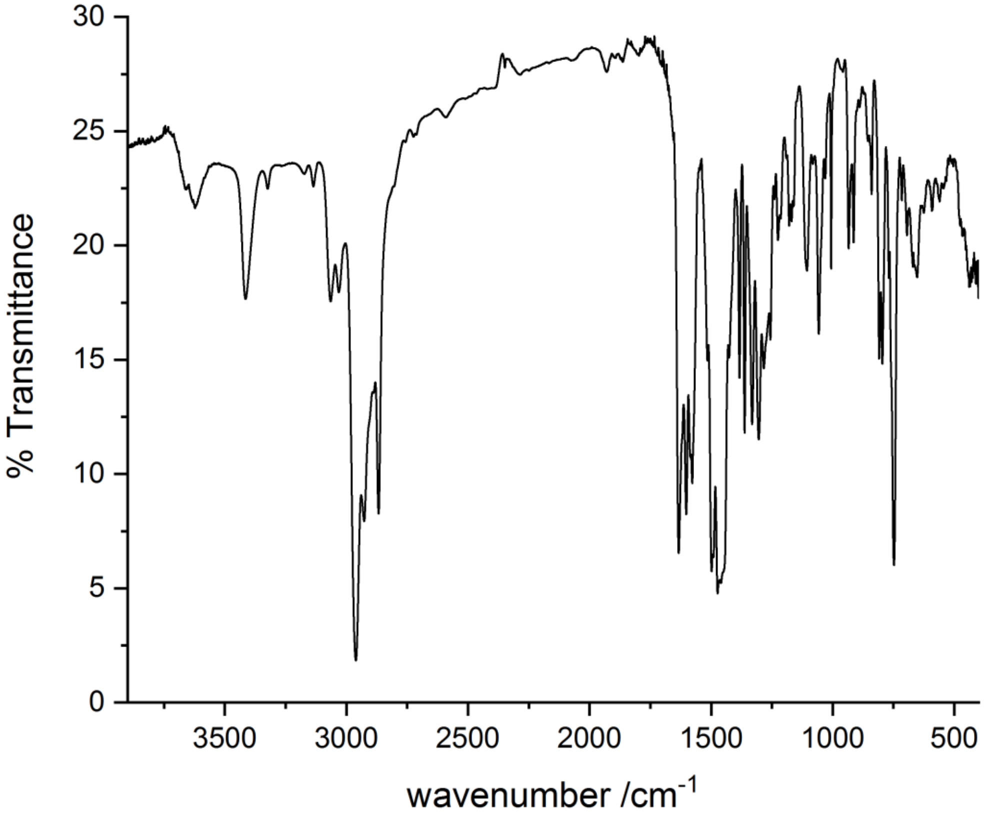

Figure SI15. IR spectrum (KBr pellet) of **1**·DME.

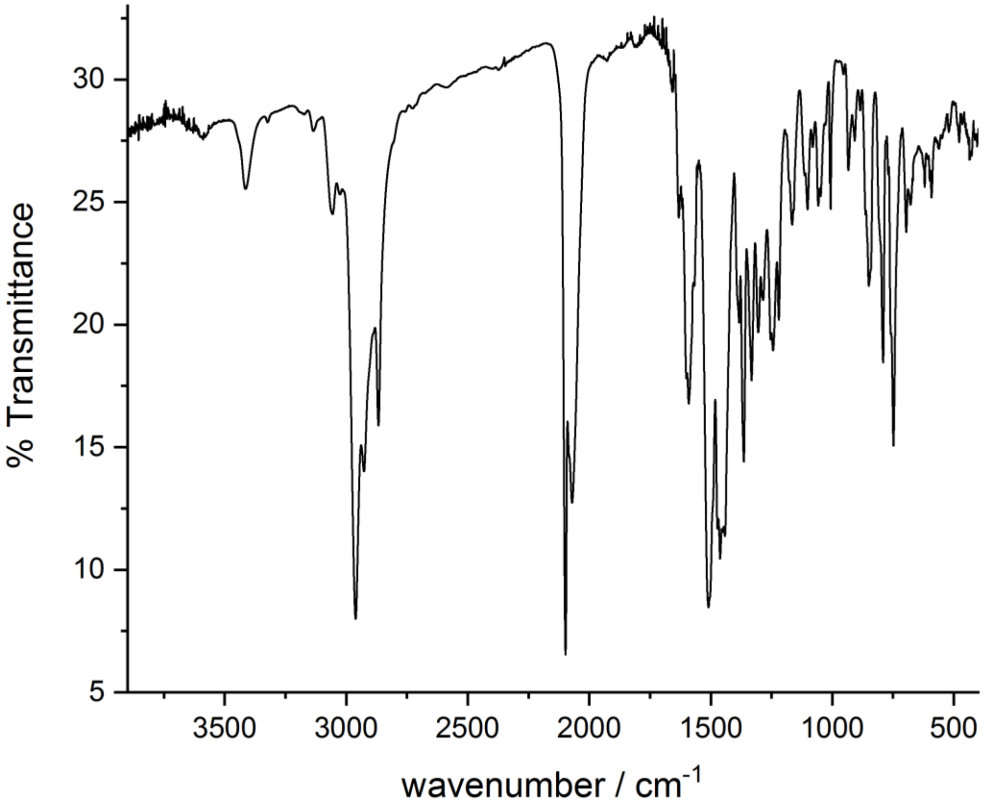

Figure SI16. IR spectrum (KBr pellet) of **2**·C_6H_6.

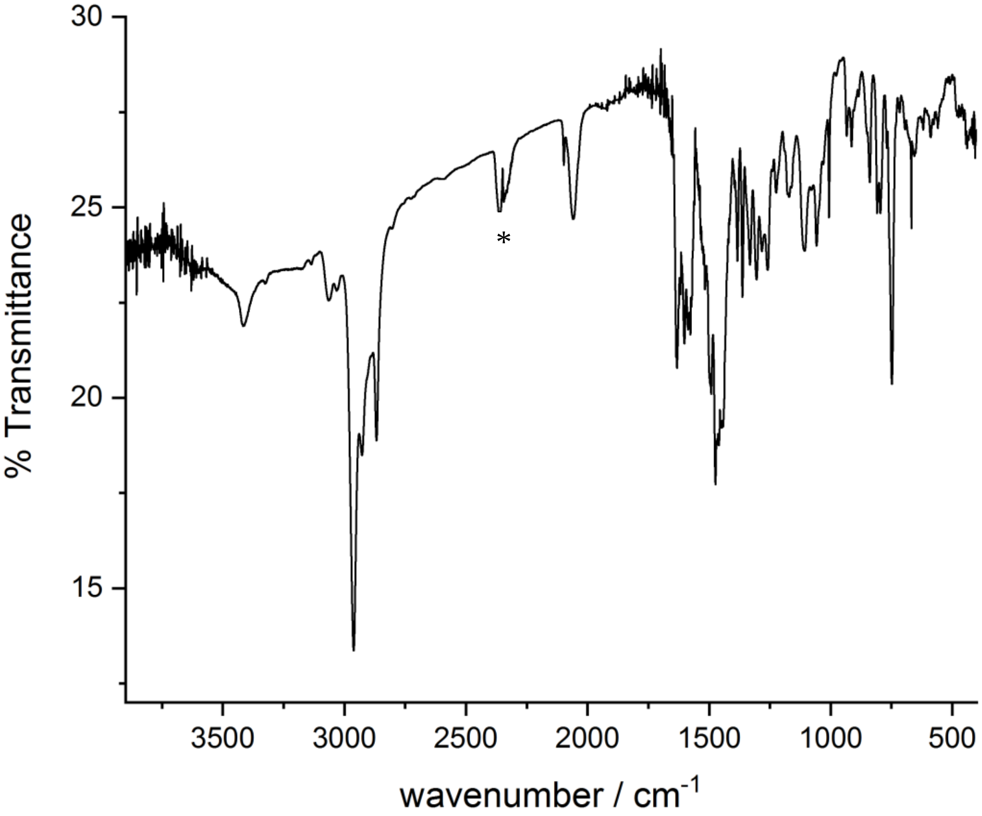

Figure SI17. IR spectrum (KBr pellet) of **3**·C_6H_{14}. Asterisk denotes CO_2 peak from incomplete background subtraction.

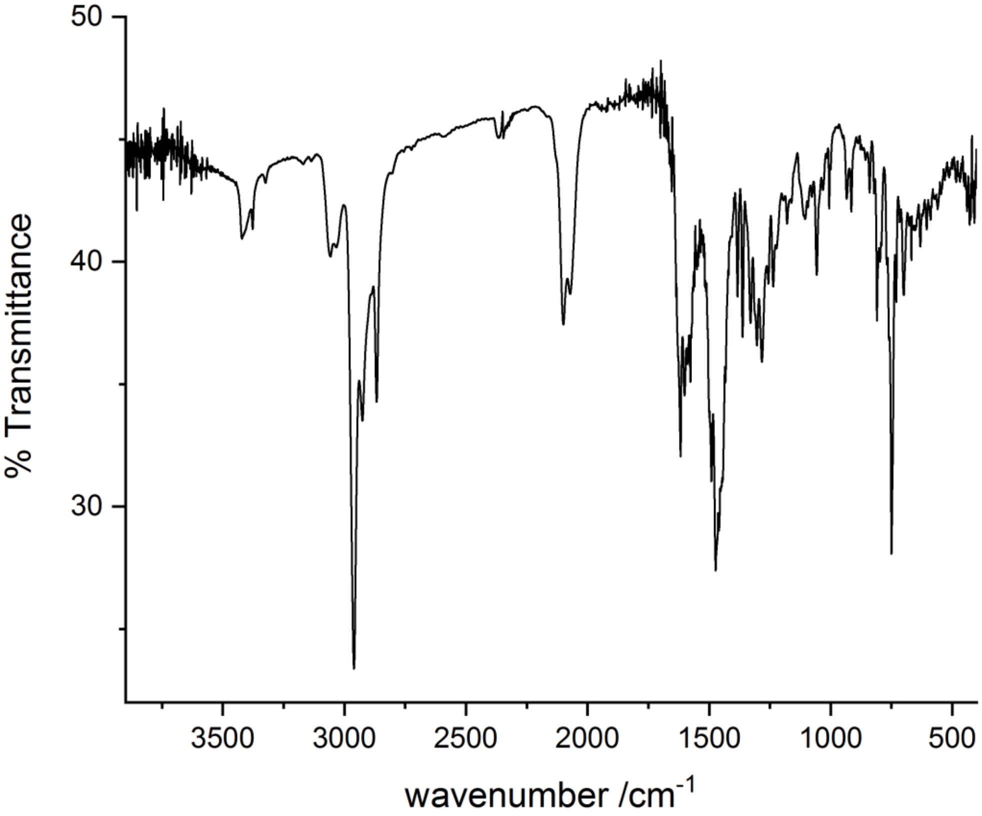

Figure SI18. IR spectrum (KBr pellet) of **5**·Et_2O.

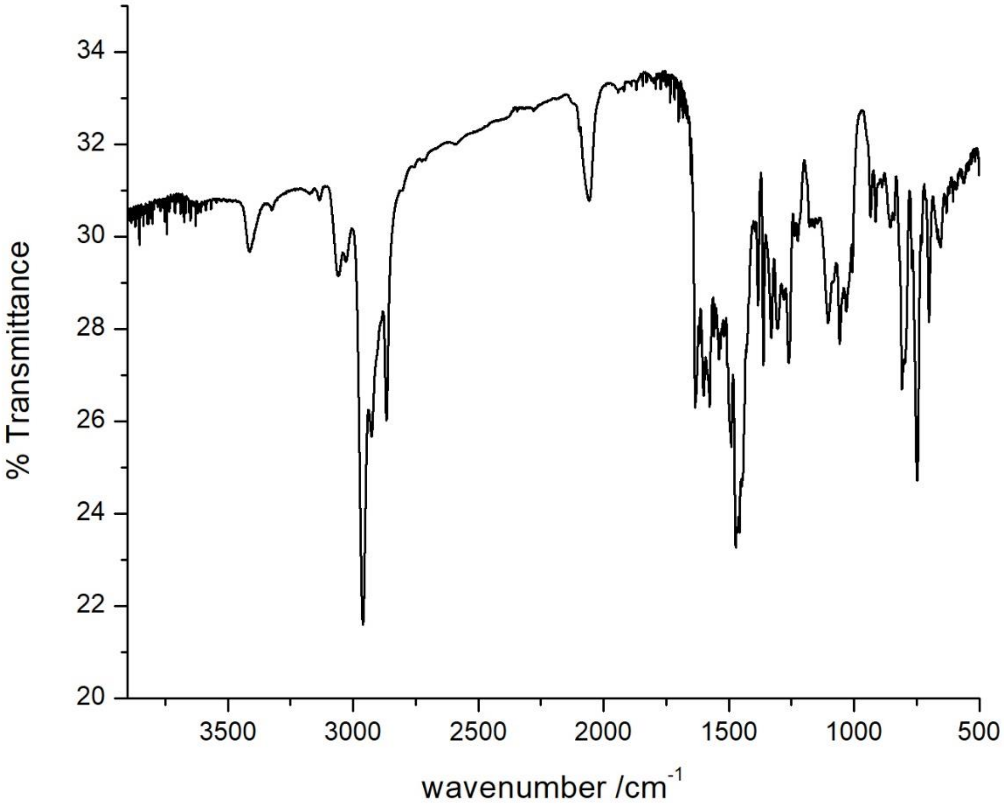

Figure SI19. IR spectrum (KBr pellet) of **6**·Et_2O.

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